

Anomalous pressure dependence of the atomic displacements in the relaxor ferroelectric $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$

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The crystal structure of the $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ (PMT) relaxor ferroelectric was studied under hydrostatic pressure up to ~ 7 GPa by means of powder neutron diffraction. We find a drastic pressure-induced decrease of the lead displacement from the inversion centre which correlates with an increase by ~ 50 % of the anisotropy of the oxygen temperature factor. The vibrations of the Mg/Ta are, in contrast, rather pressure insensitive. We attribute these changes being responsible for the previously reported pressure-induced suppression of the anomalous dielectric permittivity and diffuse scattering in relaxor ferroelectrics.

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$\text{AB}_x\text{B}'_{1-x}\text{O}_3$ complex perovskites are model compounds for the study of ferroelectricity in disordered crystals. In many of these compounds ferroelectricity occurs without a well-defined structural phase transition, and consequently they are referred as relaxor ferroelectrics, or simply relaxors [1]. Relaxors have a frequency dependent peak in the dielectric permittivity which typically extends over hundreds of degrees Kelvin. In addition, many physical properties of relaxors exhibit anomalies in this temperature range attributed to a so-called "diffuse phase transition". Despite numerous studies, the physics of systems exhibiting diffuse phase transitions is not well understood yet.

In the course of recent studies on the typical relaxor ferroelectrics $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) and $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ (PMT) a close relation between the temperature behavior of (i) the diffuse scattering, (ii) the dielectric response and (iii) the amplitude of the displacements of Pb ions from the special Wyckoff positions in the perovskite structure [2, 3] has been found. Specifically, it was observed that the susceptibility of the dynamic (quasi-elastic) component of the diffuse scattering in PMN follows well the peak of the dielectric permittivity [2] and that the intensity of the diffuse scattering in PMT matches closely the amplitude of the Pb displacements [3].

Most of the studies on relaxor ferroelectrics have concentrated on temperature and electric-field effects. Recently, interest in the properties of the relaxors under hydrostatic pressure has aroused [4, 5, 6, 7, 8, 9, 10]. Hydrostatic pressure applied to relaxors usually causes: (i) the suppression of the peak in the dielectric permittivity, as found, *e.g.*, in PMN [9] or in $\text{PbIn}_{1/3}\text{Nb}_{1/2}\text{O}_3$ (PIN) [5] and (ii) the decrease in the intensity of the diffuse scattering as observed also, *e.g.*, in PMN [10] and PIN [6]. However, up to now there exists no attempt to link these two effects to the underlying structural changes

in these systems.

Here we present a detailed structural investigation under pressure, aimed to clarify the microscopic origin for the anomalous pressure effects reported in relaxors. We applied neutron diffraction taking advantage of a better sensitivity on the oxygen position as compared to X-ray studies. The experiments were carried out on PMT, which at ambient pressure, shows a broad frequency-dependent anomaly of the dielectric response with a maximum at a frequency of 10 kHz in the vicinity of 170 K [1]. In the entire range of temperatures and applied electric fields, the symmetry of PMT is known to remain cubic (space group $\text{Pm}\bar{3}\text{m}$) [1, 3, 11].

The powder diffraction experiment was carried out at ambient temperature on the multi-detector high-resolution powder diffractometer HRPT [12] at the spallation neutron source SINQ [13] (Switzerland). Measurements were performed with a neutron wavelength of $\lambda = 1.494$ Å. Typical exposure times were ~ 15 hours. The polycrystalline sample of PMT had a volume of ≤ 100 mm³ and was loaded into an encapsulated zero-matrix TiZr gasket [14] with a deuterated methanol-ethanol (4:1) mix as a pressure-transmitting medium thus enabling hydrostatic pressure conditions up to the highest investigated pressure of ~ 7 GPa. To apply pressure, the VX3 version of the Paris-Edinburgh press [15] was used. A detailed description of this opposed-anvil set-up is given in Ref. [16]. The values of the applied pressure were estimated to better than ± 0.2 GPa from the change in the unit cell volume of PMT. To this end the third-order Birch-Murnaghan equation of state [17] was used with parameters taken from Ref. [10].

The crystal structure was refined with Fullprof [18] following a structural model of PMT developed in Ref. [3]. This study established that the structure is best described by Pb ions displaced along the $\langle 1\ 1\ 0 \rangle$ direction from the $(0\ 0\ 0)$ special position. The temperature

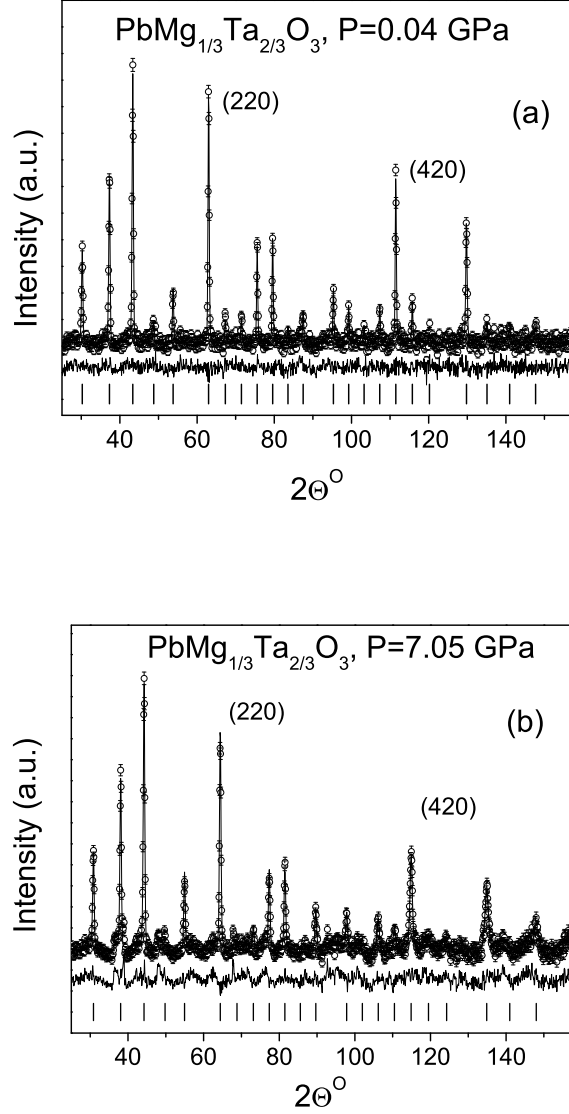


FIG. 1: Neutron powder diffraction patterns of PMT collected at nominal pressures of (a) $P=0.04$ GPa and (b) $P=7.05$ GPa. Observed data points with background originating from the pressure cell subtracted, calculated profiles and difference curves are shown. The row of ticks corresponds to the calculated positions of diffraction peaks. The peak in the vicinity of $2\theta = 45^\circ$ which is not fitted well within our model is due to scattering from a impurity of pyrochlore [3].

factors of all ions are assumed to be isotropic with the exception of the oxygen ions where anisotropic components are considered too. For the Mg/Ta ions we assume a random occupation of the Mg/Ta ions over the B-sites (0.5 0.5 0.5) of the PMT perovskite structure according to the stoichiometric ratio. To avoid unwanted correlation between the refined values of the displacement am-

plitudes and the B- factor of Pb, latter was fixed to a value of 1.14 \AA^2 obtained at $T = 300 \text{ K}$ [3]. We note that we cannot rule out a displacement of the Mg/Ta or oxygen ions but assert these displacements to be small in comparison to the temperature factors [3].

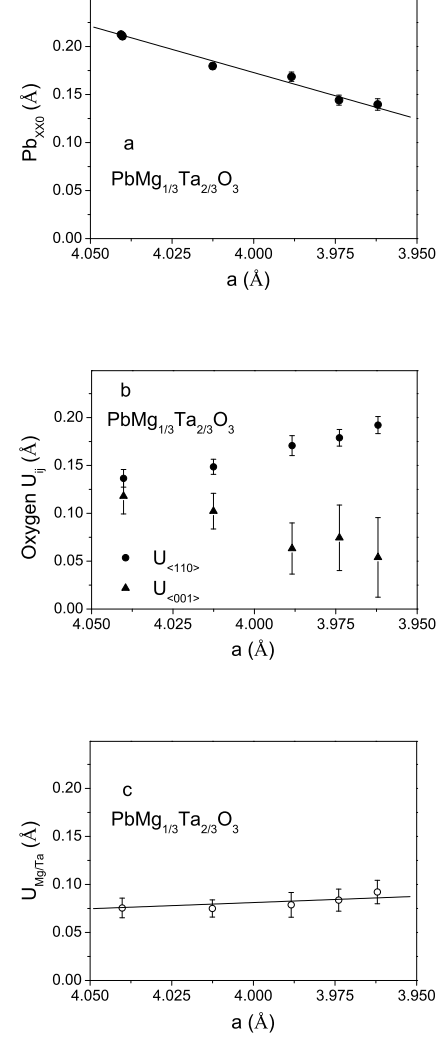


FIG. 2: (a) Dependence of the amplitude of lead displacements $Pb_{\langle xx0 \rangle}$ in PMT against lattice parameter. (b) Root mean square displacements of the oxygen ions against lattice parameter: note that the $\langle 110 \rangle$ ($\langle 001 \rangle$) direction points toward Pb (Mg/Ta). (c) Root mean square displacements of the Mg and Ta ions against lattice parameter. All graphs have the same scale to emphasize the significant difference in the pressure dependences of these parameters. Values of corresponding pressures can be extracted from Table I.

Figure 1 shows representative observed and calculated diffraction patterns obtained for PMT close to ambient and at the highest pressure of nominally $P = 7.05$ GPa. Apart from the trivial shift of all peaks to higher scattering angles related to the contraction of the PMT lattice,

TABLE I: Pressure, lattice parameter and amplitude of lead displacement of PMT (equation of state with $B = 104$ GPa, $B' = 4.7$ taken from [10]).

Pressure (GPa)	Lattice parameter (Å)	Pb displacement (Å)
0.04	4.04019(7)	0.211(3)
2.28	4.01260(7)	0.180(3)
4.47	3.98822(9)	0.169(5)
5.86	3.9738(1)	0.144(5)
7.05	3.9620(2)	0.140(6)

the effect of pressure is to modify significantly the relative peak intensities, as seen for example on the (220) and (420) reflection. Latter effect results from an isostructural displacements of the ions within the unit cell and which may be rationalized by a Rietveld analysis of the data.

Figure 2 shows the evolution of the lead displacements ($\text{Pb}_{\langle\text{XX}0\rangle}$) and the root mean-square (RMS) displacements of Mg/Ta and oxygen in PMT as a function of the lattice parameter [19]. These quantities vary approximately linearly with the lattice parameter, however, with opposite slopes and with different rates: e.g., whereas the displacement of $\text{Pb}_{\langle\text{XX}0\rangle}$ *decreases* by about 0.07\AA as the lattice contracts, the RMS of the Mg/Ta ions *increases* by about 0.02\AA . It is worth noting that all observed changes in the $\text{Pb}_{\langle\text{XX}0\rangle}$ displacements and RMS displacements of the other ions (e.g. Mg/Ta, 20%) are considerably larger than that of the cell volume of PMT ($\sim 6\%$).

Further inspection of Fig. 2 shows that the decrease in the $\text{Pb}_{\langle\text{XX}0\rangle}$ is accompanied by an increase in the anisotropy of the oxygen temperature factor. However, a reliable analysis of the components of the anisotropic temperature factors requires high statistical quality of the data. This is hardly achieved in the present experiment under high pressures and correspondingly small sample volumes. Thus, in order to analyze unambiguously the change in the anisotropy of the oxygen vibrations we have combined earlier temperature dependent studies of the PMT structure [3] with the present results. It turns out that the amplitude of the $\text{Pb}_{\langle\text{XX}0\rangle}$ is a suitable variable common to both the pressure- and the temperature-dependent studies. Figure 3 thus shows the components of the oxygen thermal ellipsoid in relation to the amplitude of Pb displacements. It is clearly seen that the $\langle 110 \rangle$ and $\langle 001 \rangle$ components of the oxygen temperature factor evolve in the opposite direction: whereas the component directed along the Pb-O bond increases significantly as the amplitude of the Pb displacements decreases, the component directed along the Mg/Ta-O bond exhibits a slight decrease. In fact, the latter component of the oxygen temperature factor is the only structural parameter which has a similar relative change as the PMT cell volume.

The above evidenced pressure-induced changes of the temperature factors in PMT are by far anomalous and may be contrasted to what is expected for a simple solid. In the latter case the temperature factors are related with the phonons and thus should decrease with increasing pressure at a rate of approximately the average Grüneisen-parameter, that is close to 1. This implies the relative change of the temperature factors to scale with the change in the unit cell volume. Obviously, the corresponding changes in PMT are in excess to such scaling and even show opposite trends for Mg/Ta and for one of the components of the oxygen temperature factors.

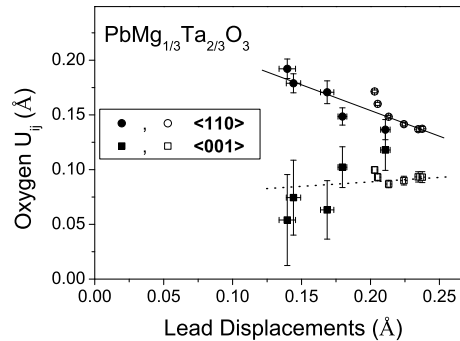


FIG. 3: Components of the oxygen thermal ellipsoid versus the amplitude of lead displacements. Data points shown by open symbols are taken from earlier temperature-dependent studies of the structure of PMT [3] at ambient pressure. These points were measured at $T=588, 450, 300, 200, 85$ and 1 K correspondingly. We note that smaller Pb displacements correspond to higher temperatures.

Due to the fact that the perovskite-type materials constitute a significant part of the earth mantle, their properties under high pressure are widely studied. However, we are not aware that substantial changes of the atomic temperature factors in these compounds have been reported before. E.g., the temperature factors of the ions in GdAlO_3 and GdFeO_3 crystals do not change significantly up to pressures of about 8 GPa [20]. The relative changes of the atomic positions in these materials all scale well with the changes in the unit cell volume.

On the other hand, it is known that hydrostatic pressure suppresses the ferroelectric properties in perovskites [21]. For example, at sufficiently high pressures BaTiO_3 [22] and KNbO_3 [23] restore the paraelectric cubic structure [24]. However, even such significant changes are not accompanied by profound changes in the temperature factors. In the case of the tetragonal-to-cubic pressure-induced phase transition of BaTiO_3 there is a shift of the Ti ion by $\sim 0.02\text{\AA}$ and the temperature factor of Ti increases by a factor of 2, whereas the structure parameters of the other ions remain essentially un-

changed [22].

From the discussion above we conclude that the pressure-induced changes in the structural parameters of PMT are a peculiarity of relaxors. The most significant of these changes are the decrease of the amplitudes of Pb displacements and the increase of the component of the anisotropic temperature factor of oxygen ions directed toward Pb. On the other hand, the change in the temperature factor of Mg/Ta is pronounced much less. From the analysis of the Bragg peak intensities we cannot infer direct information about the short-range correlations between the displaced ions. However, it is reasonable to expect that as the value of the ionic displacements decreases, the associated short-range order diminishes, which in turn causes (i) the reduction of the diffuse scattering and (ii) the suppression of the dielectric permittivity peak. Thus, our observations give a microscopic explanation for the fore-mentioned suppressions in lead-containing relaxors, namely by the anomalous correlated displacements of the lead and oxygen ions. A quantitative model to describe such relationship is a matter of future theoretical and experimental studies. High pressure measurements of the diffuse scattering using single crystals would be highly desirable.

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